Pyrolysis of Woody Biomass

Gareth Mayhead, Rebecca Snell, John R. Shelly
University of California Berkeley

Pyrolysis is the thermal decomposition of a substance that occurs in the absence of air or oxygen, and is the first step of all combustion and gasification processes. Pyrolysis can convert woody biomass into charcoal, liquid oils and gases. It is potentially an effective way to reduce bulky biomass into an energy dense, uniform and easily transportable fuel. Pyrolysis processes have an array of names including slow pyrolysis, torrefaction, torification, airless drying, destructive distillation, fast pyrolysis and flash pyrolysis. There are broadly three types of pyrolysis: slow, mild and fast. These are compared in Table 1. Each process occurs under different conditions and forms different end products.

Table 1: Types of pyrolysis, terms used, products and development status of the

technology

Pyrolysis Type	Terms Used	Temperature	Residence Time	Primary Products	Status
Mild	Torrefaction, torification, airless drying, destructive distillation*	400-600°F (200-315°C)	Short (5-30 minutes)	Torrified wood ('bio-coal')	Demonstration projects
Slow	Charcoal making, carbonnization	550-750°F (300-400°C)	Long (hours- days)	Charcoal ('biochar').	Commercially deployed
Fast	Fast pyrolysis, flash pyrolysis	750-1100°F (400-600°C)	Short (<1 second)	Liquid ('bio- oil'), char ('bio-char'), gases (H ₂ , CH ₄ , CO & CO ₂). Liquid smoke.	Demonstration projects for energy products. Commercially deployed in the food industry.

^{*} referred to as torrefaction and torrefied wood in the rest of this document

Pyrolysis Products

The three main product categories of pyrolysis processes are solids (char, torrefied wood and charcoal), tar (sometimes called bio-oil) and a mixture of gases. The products are produced in different ratios depending on the reaction type and time, temperature, feedstock composition and size.

Torrefied wood ('bio-coal')

This is a product of mild pyrolysis processes. The biomass feedstock is thermo-chemically modified in the process which changes its properties. It has less mass that the biomass feedstock meaning that it is cheaper to transport. Other characteristics mean that it could be used as a direct substitute for coal in power plants. These include a higher energy density (10,500 BTU/lb vs 8,500 BTU/lb for wood), hydrophobicity allowing storage outside, and the ability to pulverize the material permitting grinding in coal processing equipment.

Charcoal ('biochar')

Charcoal has been made from wood for thousands of years using slow pyrolysis processes. It is a black, porous, carbonaceous material made up of 85 to 98% carbon. It may be produced in lump (formed from solid wood pieces) or briquette form (formed from small charcoal particles and other additives to enhance bonding and combustion). All pyrolysis processes form some type of char product. Char comprises inorganic materials and unconverted organic solids. It has high ash and alkali content which when combusted can lead to problems of slagging and corrosion in boilers.

Liquid ('bio-oil')

Bio-oil is a mix of organic components with a high water (15-35%) and oxygen content (35-40%). Because of the high water and oxygen content Bio-oil has a relatively low heating value – 50% of conventional fuels [1]. It is acidic (pH 2-3, mainly acetic and formic acids) and therefore highly corrosive which also limits potential applications. It is not as stable in storage as fossil fuels. Viscosity and molecular weight increase with time and phase separation may occur. It is not possible to directly mix it with hydrocarbon based fuels [2].

Gases

Condensable gases (organic vapors consisting of fragmented lignin, cellulose and hemicelluloses) that are cooled rapidly form the bio-oil in fast pyrolysis. Non-condensable gases from pyrolysis include hydrogen, methane, carbon monoxide and carbon dioxide. It is possible to produce large volumes of hydrogen in preference to oil by optimizing conditions to high temperature, high heating rate and long vapor phase residence time [3, 4]. Catalysts can boost the hydrogen yield. Common ones are nickel, potassium, calcium and magnesium based. Steam reforming of vapors and water-gas shift reaction can further increase hydrogen production [5, 6]. It is also possible to produce hydrogen from bio-oil or just the water soluble fraction [1, 5].

Status of Technology

Table 1 shows the current development status of the technology. The majority of the processes are not yet commercially deployed or proven. Slow pyrolysis, which mainly represents traditional charcoal production, is commercially deployed. The only commercial deployment of fast pyrolysis is in the food industry for the production of liquid smoke from hardwood sawdust (http://www.redarrowusa.com).

A consortium of two large forest products companies in Finland (Metso Oy and UPM Oy), and a private Finland research organization (VTT Technical Research Center) have developed a large scale, integrated pilot pyrolysis facility in Tampere, Finland that is linked to an existing biomass power plant with a bubbling fluidized bed boiler.

Selected companies working on pyrolysis technologies in the USA include Dynamotive, Ensyn, Advanced Biorefinery, Renewable Oil International and Renewable Fuels Technology. It is likely to be at least 5 years before technologies are commercially ready.

Feedstock Requirements

Feedstock requirements are process specific. Slow and mild pyrolysis processes are relatively feedstock flexible and may use anything from woodchip to cordwood sized material. Fast pyrolysis processes generally have a very tight feedstock specification requiring clean and dry wood (<10% moisture content) particles of a small size (1/16-1/8" in the largest dimension).

Process and Equipment

All pyrolysis processes are endothermic requiring heat energy to drive the reaction. The heat source may be external (eg, an electric heating coil or propane burner) or it may be internally supplied (eg by combusting a portion of the feedstock or the liquids or gases produced). On heating, energy transfers to the surface of the biomass particles and then penetrates within the particles. The heat breaks the chemical bonds within the particle and the biomass degrades into its constituent parts (depolymerized and fragmented lignin, hemicellulose, cellulose, and extractive fractions) [7]. The products of pyrolysis processes are solids (charcoal), gases and organic condensable vapors. The mix of products is dependent upon pyrolysis type and process parameters. Table 2 summarizes the approximate product yields for pyrolysis processes. Slow pyrolysis results in mainly char (charcoal) formation whereas the object of fast pyrolysis is to maximize the vaporization of the wood particles to give high yields of liquids (bio-oil). This can be up to 80% of the mass of the starting material, but most commonly is between 65-75% (dry weight basis) [8]. In fast pyrolysis the char is usually separated from the hot gas/vapor stream whilst passing through a cyclone; the gases then enter a cooling chamber where they condense rapidly to form dark single-phase bio-oil or are collected as non-condensable gases (hydrogen, methane, carbon monoxide and carbon dioxide). Many different types of reactor have been designed and developed from laboratory to commercial scale [8]. The operating requirements such as particle size and mechanisms for heat transfer differ and significantly influence the output products.

Table 2: Product yields from different pyrolysis processes.

Dimolissia Timo	Product Yield			
Pyrolysis Type	Liquid	Solids	Gas	
Mild	~11%	70-90%	~2%	
Slow	30%	35%	35%	
Fast	75%	12%	13%	

Adapted from references [9], [10] and [11]

Typical Scale

Slow pyrolysis units range from small scale retort kilns producing 60 tons a year of charcoal to factories producing over 10,000 tons per year of charcoal. Mild and fast pyrolysis units are not yet commercially proven and may also come in a range of sizes depending upon technical and economic factors. There is interest in everything from small scale (350 tons per year) distributed production to large scale facilities (50,000 tons per year and above).

Product Uses and Markets

Torrefied wood

The growth in co-firing of biomass with coal over the past 10 years has led to significant interest in this product as a potential substitute for coal. It is an attractive proposition for coal power plants as torrefied wood has coal-like characteristics meaning that no modification to storage, handling or combustion equipment is required. Currently this is an immature market with research and small scale trials moving forward. Major challenges will include producing the requiring volume of material at a price that is competitive.

Charcoal

Charcoal (lump or briquette) is typically used in home barbeques and sometimes in restaurants. Charcoal was used as a soil improver in the Amazonian Basin thousands of years ago and played a part in creating the fertile "Terra Preta" soils. Research continues on the use of charcoal as a soil improver to increase water holding capacity, cation exchange and encourage microbial growth and ultimately increase soil organic matter [12, 13]. Charcoal is also used as a substitute for vermiculite, a growth media [14]. Other more specialized uses for charcoal include artist's charcoal, a fuel for gasifiers, ingredients for pharmaceuticals and make-up, animal feed, pyrotechnics, explosives, pigments and others.

A related product to charcoal is activated carbon where the process objective is to open up the carbon structure to increase the surface area available to hold (adsorb) molecules and other substances. Superheated steam is used to heat charcoal around 1470°F (800°C) to remove tars and other contaminants from the carbon structure. The charcoal used needs to have a low ash and a low volatile content meaning that clean wood is required as a feedstock (no bark, foliage or dirt). Activated carbon is used in filtration applications and can be reactivated and used again. Prices for charcoal vary according to product quality and end-use.

Bio-oil

There is potential to substitute bio-oil for conventional fuels in boilers, internal combustion engines and turbines. Trials have shown that substitution is possible but there is the potential for equipment damage due to its acidity and modifications are required [1] [15] [16]. Additionally ignition problems have been observed. The majority of engine and turbine manufacturers do not warrant the use of bio-oil. In order to effectively use bio-oil it requires further refining.

Pyrolysis Mayhead et. al.

Chemicals such as acetic acid, methanol and acetone may be recovered from the product, but are currently produced more cheaply from fossil fuels [1]. Bio-oil from a fast pyrolysis process is processed into liquid smoke, a food flavoring, by Red Arrow Products and this may be the only commercially deployed use of bio-oil.

Gases

Gases are generally either condensed into bio-oil or are combusted as part of the pyrolysis process. Hydrogen could be used in fuel cells for transportation but this is currently an undeveloped market.

Adhesives

Products in the water-insoluble fraction can be used to replace phenol in adhesives [1] for use in the manufacture of composite panel boards.

Opportunities to Use Woody Biomass in California as a Feedstock for Pyrolysis Processes

There are currently no large scale pyrolysis facilities in California. There are a number of technology developers in the state working on mild pyrolysis equipment (e.g., Renewable Fuel Technology). Small scale demonstrations of pyrolysis technologies are planned in a number of areas. Some activated carbon facilities do exist but they purchase charcoal rather than woody biomass. Therefore the short term opportunities for utilization of woody biomass by pyrolysis based technologies are extremely limited. In the longer term (5+ years) as technologies and markets mature, opportunities for the products of woody biomass pyrolysis may develop.

List of References

- 1. Czernik, S. and A.V. Bridgwater. 2004. Overview of applications of biomass fast pyrolysis oil. Energy & Fuels. 18(2):590-598.
- 2. Oasmaa, A., E. Kuoppala, and Y. Solantausta. 2003. *Fast pyrolysis of forestry residue*. 2. *Physicochemical composition of product liquid*. Energy & Fuels. 17(2):433-443.
- 3. Demirbas, A. 2009. *Hydrogen-rich Gases from Biomass via Pyrolysis and Air-steam Gasification*. Energy Sources Part a-Recovery Utilization and Environmental Effects. 31(19):1728-1736.
- 4. Demirbas, A. 2009. *Pyrolysis Mechanisms of Biomass Materials*. Energy Sources Part a-Recovery Utilization and Environmental Effects. 31(13):1186-1193.
- 5. Ni, M., Leung, D.Y.C., Leung, M.K.H., and Sumathy, K. 2006. *An overview of hydrogen production from biomass*. Fuel Processing Technology. 87:461-472.
- 6. Czernik, S., Evans, E., and French, R. 2007. *Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil.* Catalysis Today. 129:265-268.
- 7. Venderbosch, R.H. and W. Prins. 2010. *Fast pyrolysis technology development*. Biofuels Bioproducts & Biorefining-Biofpr. 4(2):178-208.
- 8. Bridgwater, A.V. and G.V.C. Peacocke. 2000. *Fast pyrolysis processes for biomass*. Renewable & Sustainable Energy Reviews. 4(1):1-73.
- 9. Anon. 2011. *IEA Bioenergy: Task 34 Pyrolysis*. [IEA Technology Network web page]. Accessed May, 2011. [Internet]. http://www.pyne.co.uk/index.php?_id=76.

- 10. Bergman, P.C.A. and J.H.A. Kiel. *Torrefaction for biomass upgrading*. In Proceedings of the 14th European Biomass Conference and Exhibition, 2005. ed. Paris, France. Energy Research Centre of the Netherlands.
- 11. Kongkeaw, N. and S. Patumsawad. *Thermal upgrading of biomass as a fuel by torrefaction*. In: IPCBEE. In Proceedings of the 2nd International Conference on Environmental Engineering and Applications, 2011. ed. Shanghai, China. IACSIT Press.
- 12. Jones, D.L., Murphy, D.V., Khalid, M., Ahmad, W., Edwards-Jones, G. and DeLuca, T.H. 2011. *Short-term biochar-induced increase in soil CO2 release is both biotically and abiotically mediated.* Soil Biology and Biochemistry. 43:1723-1731.
- 13. Streubel, J.D., Collins, H.P., Garcia-Perez, M., Tarara, J., Granatstein, D. and Kruger, C.E. 2011. *Influence of contrasting biochar types on five soils at increasing rates of application*. Soil Science Society of America Journal. 75(4):1402-1413.
- 14. Anon. 2011. Cal-Forest Nursery. personal communication.
- 15. Zhang, Q., J. Chang, T.J. Wang, and Y. Xu. 2007. *Review of biomass pyrolysis oil properties and upgrading research.* Energy Conversion and Management. 48(1):87-92.
- 16. Vamvuka, D. 2011. *Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes An overview.* International Journal of Energy Research. 35:835-862.